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PROCESS FOR PURIFYING GAS CONTAINING CYANIDES AND NITROGEN OXIDES
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1. Title

Process For Purifying Gas Containing Cyanides And Nitrogen Oxides

2. Claims

(1) A process for purifying a gas containing cyanides and nitrogen oxides comprising a step of bringing a gas containing cyanides and nitrogen oxides into contact at an elevated temperature with a catalyst that contains chromium or copper oxide and titanium oxide as the principal active components.

(2) The process for purifying a gas containing cyanides and nitrogen oxides stated in Claim 1, wherein the catalyst further contains oxide of a minimum of one metal selected from a group consisting of iron, vanadium, and manganese.

(3) The process for purifying a gas containing cyanides and nitrogen oxides stated in Claim 1 or 2, wherein the gas containing cyanides and nitrogen oxides further contains a minimum of one kind of combustible component, such as hydrocarbon, carbon monoxide, hydrogen, and so forth, and (or) oxygen.

(4) The process for purifying a gas containing cyanides and nitrogen oxides stated in any of Claims 1 through 3 comprising a step of bringing a gas containing cyanides and nitrogen oxides into contact with a catalyst that contains chromium or copper oxide and titanium oxide as the principal active components and a subsequent step of

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bringing the gas into contact with a complete oxidation catalyst in the copresence of oxygen.

3. Detailed Description of the Invention

The present invention pertains to a process for purifying a gas containing cyanides and nitrogen oxides. In particular, it pertains to a process for purifying a gas containing cyanides and nitrogen oxides that brings a gas containing cyanides and nitrogen oxides into contact with a specific catalyst and thereby efficiently decreases and detoxifies the cyanides and nitrogen oxides in said gas.

The waste gas to which the process of the present invention is applicable is not specifically limited, and examples thereof include waste gases generated from acrylonitrile manufacturing plants and electroplating plants. These waste gases contain cyanides and (or) nitrogen oxides as well as, in some cases, oxidizable (combustible) components, such as hydrocarbons, carbon monoxide, hydrogen, and so /134 forth, and, needless to say, they often contain carbon dioxide gas, oxygen, nitrogen, steam, and so forth.

Cyanides and nitrogen oxides are highly toxic, and there has been a need for establishing technology for decreasing and purifying these toxic components so as to prevent air pollution. There is, in particular, a desire for the development of a method that can treat these toxic components simultaneously.

One method employed heretofore for processing these waste gases is a direct combustion system. This system, however, requires large

combustion equipment and also occupies a large floor space.

Furthermore, this system needs to be operated at a high temperature of from 700 to 1,000 °C. Thus, this system requires high construction cost and operating cost and is not economical. Moreover, if the gas to be processed contains cyanides, they are partially or entirely converted to nitrogen oxides, which are then released directly into the atmosphere.

As another method, there is proposed a method that controls the quantity of oxygen and purifies cyanides and nitrogen oxides in a reducing ambience in the presence or absence of platinum-based catalysts (see JP-B-S53-747 and JP-A-S51-89869), but, with this method, controlling the quantity of oxygen is an essential requirement, and this method consequently has a limitation in the waste gases that it can process depending on the gas composition. Furthermore, it is difficult to apply this method to waste gases whose compositions vary extensively.

As yet another method, there is proposed a method that adds an acid to a solid or solution containing cyanides and nitrites to generate HCN and NO_x and subjects them to a gas-phase reaction at a temperature of 1400 °C or below (see JP-A-S51-40372.) This method, however, has a problem in that it requires high temperature.

As yet another method, there is proposed a method that converts cyanides in a waste gas into nitrogen oxides by the aforesaid direct combustion system and subsequently catalytically reduces said nitrogen

oxides with ammonia to detoxify them (JP-A-S51-71871.) This method, however, cannot eliminate all the disadvantageous points of the direct combustion system, and it additionally requires the use of ammonia as the reducing agent.

The present invention was achieved in view of the aforesaid situation, and its objective is to provide a process for purifying a gas containing cyanides and nitrogen oxides that brings a gas containing cyanides and nitrogen oxides into contact with a specific catalyst, thereby making it possible to efficiently decrease and detoxify the cyanides and nitrogen oxides in said gas.

Another objective of the present invention is to provide a process for purifying a gas containing cyanides and nitrogen oxides that brings a gas containing cyanides and nitrogen oxides into contact with a specific catalyst so as to efficiently reduce and detoxify the nitrogen oxides with the cyanides in said gas.

Yet another objective of the present invention is to provide a catalyst that exhibits a high activity at low temperatures and in a wide temperature range.

Yet another objective of the present invention is to provide a process for purifying a gas containing cyanides and nitrogen oxides that brings a gas containing cyanides and nitrogen oxides as well as a minimum of one kind of combustible component, such as hydrocarbon, carbon monoxide, hydrogen, and so forth, into contact with a catalyst so as to reduce and detoxify the nitrogen oxides with the cyanides in

said gas and that also brings said gas into contact with a complete oxidation catalyst so as to completely oxidize and combust said combustible component in said gas.

Furthermore, yet another objective of the present invention is to provide a process for purifying a gas containing cyanides and nitrogen oxides that brings a gas containing cyanides and nitrogen oxides as well as a minimum of one kind of combustible component, such as hydrocarbon, carbon monoxide, hydrogen, and so forth and further containing an equivalent or more amount of oxygen in relation to said combustible gas into contact with a catalyst, thereby efficiently purifying the cyanides and nitrogen oxides in said gas.

Yet another objective of the present invention is to provide a process for purifying a gas containing cyanides and nitrogen oxides that brings a gas containing catalyst poisoning components, such as sulfur compounds and the like, in addition to cyanides and nitrogen oxides, a minimum of one kind of combustible component, such as hydrocarbon, carbon monoxide, hydrogen, and so forth, and (or) oxygen into contact with a catalyst, thereby efficiently decreasing and detoxifying the cyanides and nitrogen oxides in said gas and that can improve the durability of the catalyst against said poisoning components.

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To summarize the present invention, the process of the present invention for purifying a gas containing cyanides and nitrogen oxides is characterized by including a step of bringing a gas containing

cyanides and nitrogen oxides into contact at an elevated temperature with a catalyst that contains chromium or copper oxide and titanium oxide as the principal active components.

According to the present invention, with the use of a catalyst having chromium or copper oxide and titanium oxide as the principal active components, the reduction reaction of nitrogen oxides with cyanides and the decomposition reaction of cyanides progress easily at a lower temperature than in the conventional direct combustion system. This temperature somewhat varies depending on the combination of the catalyst components used in the present invention, and approximately 450 °C or lower is high enough when a chromium-titanium catalyst is used, and approximately 350 °C or lower is high enough when a copper-titanium catalyst is used. Its applicable temperature range is also wide, approximately 200 to 450 °C with the former and approximately 150 to 350 °C with the latter, and, moreover, both catalysts make it possible to efficiently purify a gas containing cyanides and nitrogen oxides.

According to the present invention, even when a gas containing cyanides and nitrogen oxides (hereinafter simply referred to as a "waste gas") contains oxygen in a quantity (normally several %) that is tens of times the moles of the cyanides and nitrogen oxides, the reaction between the cyanides and nitrogen oxides progresses preferentially, and both components can be decreased and detoxified efficiently. Further, even when a waste gas contains more cyanides

than nitrogen oxides, because the catalyst used in the present invention additionally has an especially excellent cyanide decomposition activity, the quantity of the excess cyanides or the nitrogen oxides, which are the oxidation products of cyanides, that are released from the system is remarkably inhibited. Here, if the reaction temperature reaches approximately 400 °C or higher in the case of using the copper-titanium catalyst and 450 °C or higher in the case of using the chromium-titanium catalyst, the generation of nitrogen oxides progresses along with the oxidation of cyanides; therefore, in processing a waste gas that additionally contains a large quantity of oxygen, it is advisable to set the reaction temperature to 350 °C or lower, preferably approximately 200 to 300 °C.

The catalysts used in the present invention are not susceptible to catalyst poisoning caused by various kinds of components in the waste gas, and they exhibit particularly strong catalyst-poisoning resistance against sulfur compounds, such as SO₂ and SO₃, and are capable of maintaining their catalytic activity for a long period of time; consequently, they can be brought into direct contact with various kinds of gases to process them.

In the case of using the present invention for processing a waste gas, it is suitable for the cyanides, such as acetonitrile, acrylonitrile, and hydrogen cyanide, that are contained in the waste gas, to be present in a quantity of from 0.5 to 5 times or thereabouts,

preferably from 1 to 2 times, the nitrogen oxides (NO_x)--mainly NO and NO₂--in terms of moles.

Furthermore, in the present invention, when the spatial velocity (NTP conversion, based on an empty tower measurement, hereinafter abbreviated as "SV") of the introduced waste gas is in the range of from 1,000 to 50,000 h⁻¹, preferably from 2,000 to 30,000 h⁻¹, the cyanides and nitrogen oxides can be reacted efficiently and, thus, can be decreased and detoxified efficiently. The reaction pressure in the present invention is not specifically limited, and the atmospheric pressure or thereabouts is usually used.

Suitable as the catalysts of the present invention are those that contain part or all of the chromium or copper and titanium in the form of oxides at the end of the catalyst preparation and that contain them, with respect to the titanium-chromium catalyst, at an atomic ratio of chromium to titanium in the range of from 0.005 to 1.0, preferably from 0.02 to 0.25, to 1 and, with respect to the titanium-copper catalyst, an atomic ratio of copper to titanium in the range of from 0.02 to 1.0, preferably from 0.05 to 0.65, to 1.

In the present invention, to the principal active components of the catalysts, that is, chromium or copper oxide and titanium oxide, a small quantity of oxide of a metal, such as iron, vanadium, manganese, nickel, cobalt, molybdenum, tungsten, tin, cerium, lanthanum, bismuth, and so forth may be further added as the third component. By incorporating an oxide of a minimum of one metal selected from a group

consisting of iron, vanadium, and manganese in the catalyst as the /136 third component, the reduction reaction activity of nitrogen oxides with cyanides can be improved, and the applicable reaction temperature range can be widened.

The catalysts of the present invention can be formulated by conventionally practiced methods, including kneading, precipitation, impregnation, and so forth, but a method that can mix the catalytically active components as homogeneously and compactly as possible is suitable. As for the forming method of the catalysts, any ordinary forming technique, including an extrusion forming technique, tablet compression technique, tumbling granulation technique, and the like, can be employed.

In the present invention, the aforesaid catalytically active components may further incorporate a carrier component, such as silica, alumina, or the like. In this case, however, from the standpoint of catalytic activity and stability, it is preferable that the chromium or copper and titanium, which are the catalytically active components, and the aforesaid third component be supported in a thoroughly mixed state on the carrier. From the viewpoint of catalytic activity and catalyst poisoning resistance--especially resistance against sulfur compounds--the addition quantity of the carrier is preferably an equivalent amount or less of the titanium oxide.

As the raw material of the titanium in the catalysts used in the present invention may be used titanium oxide and titanous acid (TiO_2 .

nH_2O), titanium tetrachloride, titanium sulfate, titanyl sulfate (TiOSO_4), and so forth, which generate titanium oxide when heated, and raw materials obtained by neutralizing and precipitating aqueous solutions of titanium tetrachloride, titanium sulfate, and the like with aqueous ammonia, alkali hydroxide, alkali carbonate, or the like may also be used. Further, organic titanium compounds, such as titanium tetraisopropoxide and the like, may be used as the starting material.

When the catalysts are prepared using rutile-type or anatase type titanium oxide that is obtained by firing at a high temperature of 800 °C or higher, their purifying performance is not satisfactory. However, even with these high-temperature-processed titanium oxides, treating them with hot concentrated sulfuric acid or the like and converting part or all of the titanium oxide particles into titanium sulfate or the like makes it possible to formulate a catalyst having a higher activity.

On the other hand, as the raw material of the chromium, the present invention may use various salts thereof, such as chromium nitrate, chromium chloride, chromium acetate, and the like, and oxides thereof, such as chromium oxide and the like. As the raw material of the copper, various salts thereof, such as copper nitrate, copper sulfate, cuprous chloride, cupric chloride, copper acetate, copper formate, and the like, and oxides thereof, such as copper I oxide, copper hydroxide, and the like, can be used. Furthermore, hydroxides

obtained by neutralizing and precipitating aqueous solutions of nitrates, sulfates, chlorides, and the like of chromium and copper with alkali hydroxide, alkali carbonate, or the like can be used as the suitable starting material.

As described in the foregoing, by elucidating that a catalyst having chromium or copper oxide and titanium oxide as the principal active components exhibits excellent performance in the reducing reaction of nitrogen oxides with cyanides, the present inventors have succeeded in providing a method that is effective for the purification of various kinds of gases that contain cyanides and nitrogen oxides.

Of course, there may be cases in which the target waste gas contains either cyanides or nitrogen oxides alone, but, even in these cases--for example, in the case in which the target waste gas contains cyanides alone--the gas can be purified well according to the method of the present invention. As for a waste gas containing nitrogen oxides alone, the method of the present invention can be implemented by adding cyanides secondarily.

The aforesaid catalysts, which are the most important feature of the present invention, are capable of causing the reaction between cyanides and nitrogen oxides to progress preferentially even in a gas that contains, in addition to cyanides and nitrogen oxides, one or more kinds of combustible components, such as hydrocarbons, carbon monoxide, hydrogen, and so forth, and even in the copresence of a large quantity of oxygen; therefore, the gas can be purified by

reducing and detoxifying the cyanides and nitrogen oxides in the aforesaid gas on the aforesaid catalyst and subsequently completely oxidizing (catalytic combustion) the combustible components in the aforesaid gas on a complete oxidation catalyst positioned downstream from the aforesaid catalyst.

The present invention has the following advantages: (1) it can purify a waste gas efficiently at lower temperature compared with the direct combustion system; (2) even in purifying a waste gas containing combustible components, the reaction of cyanides and nitrogen oxides progresses preferentially, thereby making it possible to achieve the decreasing of NO_x; (3) the heat energy generated as a result of the catalytic combustion of the combustible components in a waste gas can be recovered effectively; and so forth. /137

Referring to a drawing, the following will explain the present invention by taking, as an example, the case of purifying an acrylonitrile production plant waste gas that contains cyanides and nitrogen oxides as well as carbon monoxide and hydrocarbons, such as propane, propylene, ethane, ethylene, ethane [sic], and the like.

The figure is a schematic system drawing that illustrates one concrete example of the apparatus used for implementing the present invention. In the figure, reference numeral 1 indicates a waste gas; 2, a heat exchanger; 3, a first reactor; 3', a second reactor; 4, an auxiliary fuel; 5, an auxiliary burner; and 6, secondary air. The following shows an example composition of the waste gas.

NO	200 ppm
CH ₃ CN	200 ppm
CH ₃ CHCN	30 ppm
HCN	10 ppm
CO	1.9 %
C ₁ ~ C ₄ Hydrocarbon	1.3 %
O ₂	1.3 %

In addition to these, this waste gas contains carbon dioxide gas, nitrogen, moisture, and so forth.

The waste gas (1) is introduced through the heat exchange (2) to a reactor (3) that is filled with a catalyst that is substantially composed of titanium oxide and chromium (or copper) oxide as the principal active components, and the cyanides and nitrogen oxides in the waste gas are reacted on the catalyst inside the reactor (3), thereby decreasing and detoxifying these harmful components.

If the temperature of the waste gas (1) is low, the temperature of the waste gas (1) is raised by the auxiliary burner (5), which uses the auxiliary fuel (4), such as LPG, kerosene, heavy oil, and the like, to a temperature at which the aforesaid reaction can progress (for example, to 200 °C), after which the heated gas is introduced to the aforesaid reactor (3).

When combustible components, such as carbon monoxide and hydrocarbons, are also present in a waste gas, as in waste gas 1, a reactor (3') that is filled with a complete oxidation catalyst is installed downstream from the aforesaid reactor (3), and the outlet gas from reactor 3 is introduced into reactor 3'. In this manner, the

combustible components in the gas can be completely combusted and purified.

When, as in waste gas 1, the oxygen content is insufficient compared with the oxygen quantity required for the complete combustion of the combustible components, secondary air (6) needs to be added to the waste gas (1). It is suitable for the quantity of oxygen in relation to the combustible components to be more than, preferably more than 1.1 times, the stoichiometric quantity for the complete oxidation reaction. Secondary air (6) may be added to waste gas 1 beforehand and then used for the aforesaid process. Alternatively, it may be added at a section between reactor 3 and reactor 3'.

As the complete oxidation catalyst packed inside reactor 3', any known catalyst may be used depending on the properties of the waste gas to be treated. However, in the case of treating a dirty gas that contains catalyst poisoning components, such as sulfur oxides, it is preferable to use precious metal-carrying, especially platinum-carrying, titania catalysts.

By running the outlet gas of reactor 3 through reactor 3' in this manner, heat is generated as a result of the oxidation reaction, and the temperature of reactor 3' increases to approximately 600 °C in the case of waste gas 1. By subjecting the outlet gas of reactor 3' and waste gas 1 or a mixture of waste gas 1 and secondary gas 6 to a heat-exchange treatment with the heat exchanger (2), waste gas 1 [alone or a mixture of it and secondary air (6)] to be introduced into reactor 3

can be set to a prescribed temperature, for example, to 200 °C. In this case, the auxiliary burner (5) needs to be operated only at the start up. The outlet gas of reactor 3' that has run through the heat exchanger (2) is cooled by heat energy recovery equipment or the like and subsequently released into the atmosphere. The heat energy recovery equipment may be installed upstream from the heat exchanger (2). In this case also, the outlet gas of reactor 3' runs through the heat energy recovery equipment and then undergoes a heat-exchange process with waste gas 1 [alone or a mixture of it and secondary air (6)].

As explained in the foregoing, the present invention makes it possible to efficiently purify even a waste gas that contains combustible components, such as carbon dioxide and hydrocarbons, in addition to cyanides and nitrogen oxides, thus exhibiting the effects of the present invention fully.

The following will explain the present invention in detail by presenting working examples, but the present invention is not limited to or restricted by these examples.

Working Example 1

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A slurry of metatitanic acid $[\text{TiO}(\text{OH})_2]$ was weighed to obtain 216 g of it in terms of TiO_2 and combined with 30 g chromic anhydride (CrO_3), and the mixture was kneaded thoroughly with a kneading machine by a wet method for about 3 hours. After the obtained mixture was dried at approximately 120 °C for 10 hours, it was formed into

granules having a grain size of 60 mesh pass and then combined with 2 % by weight graphite, to which mixture water was further added to adjust the water content to approximately 5 % by weight, after which the mixture was formed into tablets 5 mm in diameter and 5 mm in height under 500 kg/cm² compacting pressure. The obtained formed product was fired at 500 °C for 4 hours. The catalyst thus obtained contained titanium and chromium in the form of oxide and had a ratio of Ti: Cr = 9: 1, in terms of atomic ratio.

A quartz reaction tube having an inner diameter of 30 mm was filled with 24 ml of this catalyst, and a gas having the composition shown below was fed to the catalyst layer at a spatial velocity (SV) of 10,000 h⁻¹, thereby bringing about an NO reduction reaction with acetonitrile.

NO	200 ppm
CH ₃ CN	400 ppm
O ₂	3 %
CO ₂	12 %
H ₂ O	12 %
N ₂	the balance

NO was determined with a chemiluminescent-type NOx analyzer, and the rate of NO reduction was found by the following equation.

$$\text{Rate of NO reduction (\%)} = (1 - \text{outlet NO/fed NO}) \times 100$$

The obtained results are shown in Table 1 below.

Working Example 2

In this example, 72.5 g copper nitrate [Cu(NO₃)₂ · 3H₂O] was used in place of 30 g chromic anhydride (CrO₂), but the rest was conducted

in the entirely same manner as in Working Example 1 to prepare a catalyst. This catalyst contained titanium and copper in the form of oxide and had a ratio of Ti: Cu = 9: 1, in terms of atomic ratio.

Using this catalyst, an NO reduction reaction with acetonitrile was carried out in the same manner as in Working Example 1. The obtained results are shown in Table 1 below.

Comparative Example 1

A metatitanic acid slurry was weighed to obtain 240 g of it in terms of TiO_2 , and 5 ml of an aqueous solution (10 g Pt/100 ml) of chloroplatinic acid (H_2PtCl_6) was diluted with water and subsequently added to the aforesaid slurry. Thereafter, the wet kneading, drying, granulating, tableting, and firing were carried out in the same manner as in Working Example 1, thereby obtaining catalyst tablets 5 mm in diameter and 5 mm in height. This catalyst was reduced in a hydrogen flow at 450 °C for 3 hours, thereby obtaining a finished catalyst. This catalyst was a 0.21 % by weight platinum-titania catalyst.

Using this catalyst, an NO reduction reaction with acetonitrile was carried out in the same manner as in Working Example 1. The obtained results are shown in Table 1 below.

TABLE 1

反应温度 (a)(c)	(b) NO 还原率 (%)		
	实施例 1 (c)	实施例 2 (c)	比较例 1 (d)
150	105	520	0
200	280	460	460
250	545	625	725
300	735	810	120
350	820	880	~150
400	930	85	~1520
450	500	—	—

Key: a) reaction temperature; b) rate of NO reduction; c) working example; d) comparative example.

As seen from Table 1, although the results varied depending on the reaction temperature, the use of the catalysts of the present invention yielded good rates of reduction.

Working Example 3

Titanium tetrachloride (TiCl_4) (484 g) was dissolved in approximately 1 l distilled water. This solution was neutralized with 5N aqueous ammonia to generate a precipitate, and the generated precipitate was thoroughly washed by decantation and subsequently filtered. An aqueous solution in which was dissolved 120 g chromium nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$] and an aqueous solution in which was dissolved 17.5 g ammonium metavanadate (NH_4VO_3) together with approximately 20 g oxalic acid were added to the aforesaid precipitate, and the mixture was kneaded thoroughly with a kneading machine by a wet method for about 3 hours. After the obtained mixture was dried at approximately 140 °C for 5 hours, it was formed into granules having a grain size of 60 mesh pass and then combined with 2 % by weight graphite, to which mixture water was further added to adjust the water

content to approximately 5 % by weight, after which the mixture was formed into tablets 5 mm in diameter and 5 mm in height. The obtained formed product was fired at 550 °C for 3 hours. The catalyst thus obtained contained titanium, chromium, and vanadium in the form of oxides and had a ratio of Ti: Cr: V = 85: 10: 5 in terms of atomic ratio. /139

Except that this catalyst and a gas having the composition shown below were used, an NO reduction reaction with acetonitrile was carried out in the same manner as in Working Example 1. The obtained results are shown in Table 2 below.

NO	200 ppm
CH ₃ CN	300 ppm
SO ₂	500 ppm
SO ₃	200 ppm
O ₂	5 %
CO ₂	12 %
H ₂ O	12 %
N ₂	the balance

Comparative Example 2

To a precipitate of titanium hydroxide obtained in the same manner as in Working Example 3 were added an aqueous solution in which was dissolved 121 g iron nitrate and an aqueous solution in which was dissolved 17.5 g ammonium metavanadate together with approximately 20 g oxalic acid, and the rest was carried out in the same manner as in Working Example 3, thereby preparing a catalyst. This catalyst contained titanium, iron, and vanadium in the form of oxide and had a ratio of Ti: Fe: V = 85: 10: 5 in terms of atomic ratio.

Except that this catalyst and a gas having the same composition as in Working Example 3 were used, an NO reduction reaction with acetonitrile was carried out in the same manner as in Working Example 1. The obtained results are shown in Table 2 below.

TABLE 2

反応温度 (a) (°C)	NO還元率 (%) (b)	
	実施例 1 (c)	比較例 1 (d)
200	480	155
250	725	325
300	845	430
350	915	-520
400	845	-1240

Key: a) reaction temperature; b) rate of NO reduction; c) working example; d) comparative example.

As seen from Table 2, although the results varied depending on the reaction temperature, the use of the catalyst of the present invention yielded a good rate of reduction.

Working Examples 4 through 6

In place of 120 g chromium nitrate in Working Example 3, 72.5 g copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ was used, and, as another metal component, 61 g iron nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, 17.5 g ammonium metavanadate (NH_4VO_3) to which was added approximately 20 g oxalic acid, and 43 g manganese nitrate $[\text{Mn}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ were used individually. The rest was conducted according to the preparation method used in Working Example 3, thereby preparing three kinds of catalysts. The atomic ratio of each catalyst was: Ti: Cu: Fe = 85: 10: 5, Ti: Cu: V = 85: 10: 5, and Ti: Cu: Mn = 85: 10: 5.

Using each of these catalysts and a gas having the composition shown in Working Example 2, an NO reduction reaction with acetonitrile was carried out in the same manner as in Working Example 1. The obtained results are shown in Table 3 below.

TABLE 3

反应温度 (a) (°C)	NO 還元率 (%) (b)		
	例 4 (c)	例 5 (c)	例 6 (c)
350	81.9	70.5	72.8
300	91.9	91.8	78.8

Key: a) reaction temperature; b) rate of NO reduction; c) working example.

As seen from Table 3, although the results varied depending on the reaction temperature, the use of the catalysts of the present invention yielded good rates of reduction.

Working Example 7

Using the same catalyst as in Working Example 1 and a gas having the composition shown in Working Example 3, an NO reduction reaction with acetonitrile was carried out at a reaction temperature of 300 °C and at an SV of 5000 h⁻¹, thereby investigating the durability of the catalyst. The experiment method was in accordance with the method used in Working Example 1. The obtained results are shown in Table 4.

Comparative Example 3

Aluminum nitrate [Al(NO₃)₃ · 9H₂O] (1013 g) was dissolved in approximately 1 l distilled water. This solution was neutralized with 5N aqueous ammonia to generate a precipitate. The generated precipitate was thoroughly washed by decantation and subsequently

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filtered. To this was added 30 g chromic anhydride, and water was further added to knead the mixture thoroughly with a kneading machine by a wet method for about 3 hours. Thereafter, according to the same method as in Working Example 1, a catalyst was prepared. This catalyst contained aluminum and chromium in the form of oxides and had a ratio of Al: Cr = 9: 1 in terms of atomic ratio.

Under the same conditions as in Working Example 7, except that this catalyst was used in the present example, an NO reduction reaction with acetonitrile was carried out to investigate the durability of the catalyst. The obtained results are shown in Table 4 below.

TABLE 4

反应时间 (a)(h)	NO 還元率 (b)	
	実例 7 720 (c)	比較例 8 745 (d)
50	705	720
100	695	580
150	705	485
200	700	450

Key: a) reaction time (in hours); b) rate of NO reduction; c) working example; d) comparative example.

As seen from Table 4, the catalyst of the present invention had excellent durability against SO₂ and SO₃.

Working Example 8

Using the same catalyst as in Working Example 2 and a gas having the composition shown below, an NO reduction reaction with acetonitrile was carried out at a reaction temperature of 250 °C and

at an SV of 5000 h^{-1} , thereby investigating the durability of the catalyst.

NO	200 ppm
CH ₃ CHCN	400 ppm
SO ₂	200 ppm
SO ₃	500 ppm
O ₂	3 %
N ₂	the balance

The obtained results are shown in Table 5 below.

Comparative Example 4

Aluminum nitrate (1013 g) was dissolved in approximately 1 l distilled water, and this solution was neutralized with 5N aqueous ammonia to generate a precipitate. The generated precipitate was thoroughly washed by decantation and subsequently filtered. To this was added 72.5 g copper nitrate, and water was further added to knead the mixture thoroughly with a kneading machine by a wet method for about 3 hours. Thereafter, according to the same method as in Working Example 1, a catalyst was prepared. The obtained catalyst contained aluminum and copper in the form of oxide and had a ratio of Al: Cu = 9: 1 in terms of atomic ratio. The obtained results are shown in Table 5 below.

TABLE 5

反应時間 (時)(a)	NO 還元率 (b)	
	實例 9 (c)	比較例 1 (d)
00	930	550
100	915	485
150	915	485
200	915	485

Key: a) reaction time (in hours); b) rate of NO reduction; c) working example; d) comparative example.

As seen from Table 5, the catalyst of the present invention had excellent durability against SO_2 and SO_3 .

Working Example 9

Referring to the figure, the first reactor (3) was filled with 24 ml of the catalyst obtained in Working Example 1 and the second reactor (3') with 8 ml of the catalyst obtained in Comparative Example 1, and a purification test was carried out with a gas having the following composition.

NO	200 ppm
CH_3CN	300 ppm
C_3H_8	1.0 %
O_2	10 %
N_2	the balance

The temperature of the first reactor (3) and that of second reactor (3') were set to 300 °C with the external heating oven (electric oven), and the aforesaid gas was fed to the first reactor (3) at a flow rate of 240 Nl/hour and further sent to the second reactor (3').

The results of gas analyses at the inlet and outlet of the first reactor (3) and the outlet of the second reactor (3') are shown in Table 6.

Incidentally, acetonitrile and propane were measured by FID (Flame Ionization Detector) gas chromatography.

TABLE 6

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ガス成分 (a)	ガス濃度 (ppm 又は %) (b)		
	第1反応器入口 (c)	第1反応器出口 (d)	第2反応器出口 (e)
NO	400	20	2
CH ₃ CN	640	10	< 1
C ₃ H ₈	1.0	0.05	< 0.1

Key: a) gas components; b) gas concentration; c) first reactor inlet; d) first reactor outlet; e) second reactor outlet.

As seen from Table 6, every one of the gas components was substantially decreased.

Working Example 10

Referring to the figure, the first reactor (3) was filled with 24 ml of the catalyst obtained in Working Example 2 and the second reactor (3') with 8 ml of the catalyst obtained in Comparative Example 1, and a purification test was carried out with a gas having the following composition.

NO	400 ppm
CH ₃ CN	640 ppm
C ₃ H ₈	1.0 %
O ₂	10 %
N ₂	the balance

The temperature of the first reactor (3) and that of the second reactor (3') were set to 250 °C, and the aforesaid gas was fed to the

first reactor (3) at a flow rate of 240 Nl/hour and further sent to the second reactor (3').

The results of gas analyses at the inlet and outlet of the first reactor (3) and the outlet of the second reactor (3') are shown in Table 7.

Incidentally, acetonitrile and propane were measured by the aforesaid FID gas chromatography.

TABLE 7

ガス成分 (a)	(b) ガス濃度 (ppm 又は%)		
	第1反応器入口	第1反応器出口	第2反応器出口
HCN	400 (c)	40 (d)	17 (e)
CH ₃ CN	410	12	< 1
C ₃ H ₈	10	375	< 0.1

Key: a) gas components; b) gas concentration; c) first reactor inlet; d) first reactor outlet; e) second reactor outlet.

As seen from Table 7, every one of the gas components was substantially decreased.

As explained in the foregoing, according to the present invention, by catalytically reacting a gas containing cyanides and nitrogen oxides as well as various other kinds of compounds with a specific catalyst at low temperature, the cyanides and nitrogen oxides in said gas can be decreased and detoxified efficiently. Furthermore, even if said gas contains catalyst poisoning components, such as sulfur compounds and the like, the present invention can provide a catalyst having high durability against these poisoning components.

4. Brief Explanation of Drawing

The figure is a schematic drawing that illustrates one concrete example of the apparatus used for implementing the present invention.

1 ... waste gas

2 ... heat exchanger

3 ... first reactor

3' ... second reactor

4 ... auxiliary fuel

5 ... auxiliary burner

6 ... secondary air

